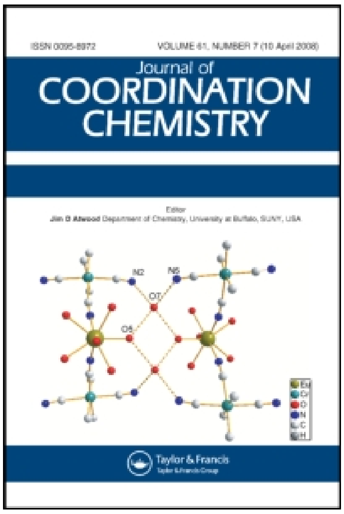

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Tatucu, Mariana , Kriza, Angela , Maxim, Catalin and Stanica, Nicolae(2009) 'Synthesis and structural studies of Co(II), Ni(II) and Cd(II) complexes with 2-acetylpyridine', Journal of Coordination Chemistry, 62: 7, 1067 — 1075, First published on: 29 July 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958970802460671
URL: http://dx.doi.org/10.1080/00958970802460671

Journal of Coordination Chemistry
Vol. 62, No. 7, 10 April 2009, 1067–1075

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Synthesis and structural studies of Co(II), Ni(II) and Cd(II) complexes with 2-acetylpyridine

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(*Received 18 April 2008; in final form 21 July 2008*)

Three new mononuclear complexes [Co(2-Acpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**1**), [Ni(2-Acpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**2**) and [Cd(2-Acpy)$_2$(NO$_3$)$_2$] (**3**) (2-Acpy = 2-acetylpyridine) have been synthesized and characterized by elemental analysis, IR and UV–Vis spectroscopy. The structures of **1** and **3** were accomplished by single crystal X-ray diffraction. Crystallographic investigation of **1** reveals monomeric, dicationic units in which the cobalt(II) ion is six-coordinate. The coordination sphere is formed by two N, O bidentate acetylpyridine ligands and two water molecules. The crystal structure of **3** consists of monomeric units in which the cadmium is eight-coordinate. Both the organic ligand and nitrate groups are bidentate chelators. The supramolecular solid-state architecture is sustained by π–π interactions.

Keywords: Crystal structure; Co(II); Ni(II); Cd(II) complexes; 2-Acetylpyridine; π–π Stacking interactions

1. Introduction

A diversity of the structures can be obtained from monomeric species to low or high-dimensionality coordination polymers from pyridine derivatives and transition metal ions. A short survey of the literature on cobalt(II) coordination chemistry reveals mononuclear compounds when the organic ligand (L) is 2-acetylpyridine [1] or pyridine betaine [2], 1-(2-pyridinyl)ethanone oxime [3], 3-methylpyridine [4], di-2-pyridyl ketone [5], as well as linear coordination polymers linked into a three-dimensional network by intermolecular hydrogen-bonding for L = 2-pyridinyl-4-pyridinylmethanone [6] or two-dimensional one for L = 4,4′-bipyridine [7]. Helical architectures have been described for L = 2-pyridinyl-3-pyridinylmethanone [8] and an azido-bridged

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802460671

disc-like heptanuclear cluster for 2-benzoyl pyridine [9]. Cadmium(II) as a d^{10} metal example contains many reports where Cd(II) in the presence of a pyridine ligand (2-acetylpyridine, 4-acetylpyridine, 2-pyridinyl-4-pyridinylmethanone) is six-coordinate [6, 10–16] and also several structures with eight-coordinate Cd(II), with alkyl-2-pyridinecarboxylate esters [17], 1,3,6,7-tetramethyllumazine [18] and 2-pyridinyl-4-pyridinylmethanone [6]. Crystal structures consist either of monomeric units [17, 18] or 2-D and 3-D networks [6, 10].

In this article we present the synthesis and structural characterization of three new complexes with 2-acetylpyridine (hereafter denoted as 2-Acpy): [Co(2-Acpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**1**), [Ni(2-Acpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**2**) and [Cd(2-Acpy)$_2$(NO$_3$)$_2$] (**3**).

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were of reagent grade and used without purification. C, H, and N elemental analyzes were performed on a Costech ECS 4010 elemental analyzer. IR spectra were recorded as KBr pellets with a Bio-Rad FTS 135 spectrometer from 4000–400 cm^{-1}. UV–Vis spectra (diffuse reflectance technique) were recorded with a VSU-2P (Carl–Zeiss Jena) spectrophotometer. The magnetic measurements were performed at room temperature using the Faraday method. Single-crystal X-ray diffraction measurements for **1** and **3** were performed on a Stoe Imaging Plate Diffraction System (STOE IPDS II) using graphite-monochromated Mo-Kα radiation.

2.2. *Syntheses*

The three compounds have been obtained following the same general procedure: to ethanolic solution (15 mL) of 2-acetylpyridine (2 mmol, 0.2422 g) was added an ethanolic solution (15 mL) containing $M(NO_3)_2 \cdot nH_2O$ [$n = 6$ for M = Co(II), Ni(II); $n = 4$ for M = Cd(II)] (1 mmol, 0.291 g, 0.2908 g, 0.3084 g). The slow evaporation of the resulting mixtures leads to single crystals for **1** and **3**, and powder for **2**.

2.2.1. [Co(2-Acpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (1). Red single crystals. Yield 77%. Anal. Calcd for $C_{14}H_{18}CoN_4O_{10}$ (%): C, 36.44; H, 3.9; N, 12.14. Found: C, 36.99; H, 4.01; N, 11.98. IR (cm^{-1}, KBr): 3216 (s), 1660 (vs), 1600 (m), 1571 (m), 1384 (vs), 1310 (s), 1096 (m), 970 (w), 781 (s), 627 (m).

2.2.2. [Ni(2-Acpy)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (2). Green crystals. Yield 65%. Anal. Calcd for $C_{14}H_{18}NiN_4O_{10}$ (%): C, 36.44; H, 3.9; N, 12.14. Found: C, 36.80; H, 4.25; N, 11.73. IR (cm^{-1}, KBr): 3225 (s), 1656 (vs), 1598 (m), 1569 (m), 1384 (vs), 1314 (s), 1101 (w), 973 (w), 792 (s), 632 (s).

2.2.3. [Cd(2-Acpy)$_2$(NO$_3$)$_2$] (3). Colorless single crystals. Yield 80%. Anal. Calcd for $C_{14}H_{14}CdN_4O_8$ (%): C, 35.14; H, 2.92; N, 11.71. Found: C, 35.89; H, 3.01; N, 11.12.

IR (cm^{-1}, KBr): 1678 (s), 1592 (s), 1569 (m), 1445 (vs), 1283 (vs), 1093 (m), 973 (m), 787 (s), 614 (s).

2.3. *Single-crystal X-ray diffraction*

Single-crystal X-ray diffraction was used for crystal structure determination of **1** and **3**. XRD data were collected on a STOE IPDS II image plate detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Data collections: Stoe X-AREA [19]. Cell refinement: Stoe X-AREA [19]. The structures were solved by direct methods and refined with anisotropic displacement parameters based on F^2 using SHELXS 97 [20] and SHELXL 97 [21]. Hydrogen atoms, except those of water, were stereochemically fixed on their ideal positions with fixed isotropic U values and their C–OH distances were refined freely. The hydrogen atoms of water were identified from the difference Fourier transform and the O–H distances were varied freely during the refinement. The crystallographic details are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

Reaction between 2-acetylpyridine and $M(NO_3)_2 \cdot nH_2O$ [$n = 6$ for M = Co(II), Ni(II); $n = 4$ for M = Cd(II)] in a 2 : 1 molar ratio leads to three new complexes: $[Co(2\text{-}Acpy)_2$

Table 1. Crystallographic data, details of data collection and structure refinement parameters for **1** and **3**.

Compound	**1**	**3**
Chemical formula	$C_{14}H_{18}CoN_4O_{10}$	$C_{14}H_{14}CdN_4O_8$
M ($g\,mol^{-1}$)	461.25	478.69
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group (Å,°)	C/c	C_2/c
a	13.3563(15)	8.6650(9)
b	8.5159(6)	15.4088(18)
c	16.5788(17)	12.9877(12)
β	93.747(9)	94.311(8)
V(Å^3)	1881.7(3)	1729.2(3)
Z	4	4
D_c ($g\,cm^{-3}$)	1.628	1.839
μ (mm^{-1})	0.975	1.316
$F(000)$	948	952
R_{int}	0.0253	0.0487
Reflections collected	7652	8330
Unique reflections	2268	4428
Goodness-of-fit on F^2	0.970	1.184
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0501, 0.0864	0.0250, 0.0630
R_1, wR_2 (all data)	0.0874, 0.0972	0.0261, 0.0635
Largest diff. peak and hole (e Å^{-3})	0.556, −0.324	0.359, −0.649

Table 2. Selected bond distances and angles for **1** and **3**.

1		**3**	
Co1–N2	2.026(8)	Cd1–N2	2.3177(15)
Co1–O2W	2.095(5)	Cd1–O1	2.3291(18)
Co1–O1W	2.124(7)	Cd1–O4	2.4919(16)
Co1–O2B	2.131(4)	Cd1–O2	2.5649(19)
Co1–N1	2.134(7)	N1–O3	1.227(3)
Co1–O2	2.136(3)	N1–O2	1.241(3)
N2–Co1–O2W	90.5(3)	N1–O1	1.261(3)
N2–Co1–O1W	90.3(3)	N2–Cd1–O4	67.85(5)
O2W–Co1–O1W	178.4(2)	O1–Cd1–O2	51.62(6)
N2–Co1–O2B	79.30(19)	O2–N1–O1	117.69(19)
O2W–Co1–O2B	90.74(18)	C1–N2–Cd1	119.00(11)
O1W–Co1–O2B	88.07(16)	C5–N2–Cd1	121.92(13)
N2–Co1–N1	178.8(2)		
O2W–Co1–N1	89.1(3)		
O1W–Co1–N1	90.0(3)		
O2B–Co1–N1	101.84(18)		
N2–Co1–O2	101.00(18)		
O2W–Co1–O2	89.89(18)		
O1W–Co1–O2	91.29(17)		
O2B–Co1–O2	179.30(18)		

$(H_2O)_2](NO_3)_2$ (**1**), $[Ni(2\text{-}Acpy)_2(H_2O)_2](NO_3)_2$ (**2**) and $[Cd(2\text{-}Acpy)_2(NO_3)_2]$ (**3**). For **1** and **3** we were able to get single crystals of appropriate quality for single crystal structure analysis.

3.2. *Description of crystal structures*

The detailed crystallographic data for **1** and **3** are listed in table 1. Selected bond lengths and angles are shown in table 2.

Complex **1** crystallizes in a *C*/*c* space group as a dication $[Co(2\text{-}Acpy)_2(H_2O)_2]^{2+}$, along with nitrate counter anions. As shown in figure 1, the cobalt(II) ion is six-coordinate, the coordination positions occupied by two N, O bidentate acetylpyridine ligands with five-membered chelate rings, and two water molecules. The two water molecules and nitrate counter anions are involved in hydrogen bonding.

The monomeric units are not centrosymmetric. The interatomic Co1–O1W distance (2.124(7) Å) is slightly longer than Co1–O2W (2.095(5) Å), while the two Co1–O2, and Co1–O2B distances and the Co1–N1 bond are almost equal (2.136(3), 2.131(4), 2.134(7) Å), only the Co1–N2 bond is shorter (2.026(8) Å). The coordination polyhedron is a slightly distorted octahedron.

Hydrogen bonding plays a very important role in the packing of this compound. As shown in figure 2, the molecular units are linked in two-dimensional networks with each coordinated water establishing two hydrogen bonds with oxygen of nitrate.

Compound **3** crystallizes in C_2/c space group as a neutral $[Cd(2\text{-}Acpy)_2(NO_3)_2]$ complex. The crystal structure consists of monomeric units, as shown in figure 3. Selected distances and angles around the metal ion are listed in table 2. The eight-coordinate Cd1 has two acetylpyridine ligands, each acting in the N2, O4-chelating mode and two bidentate coordinated nitrates, leading to a dodecahedral coordination

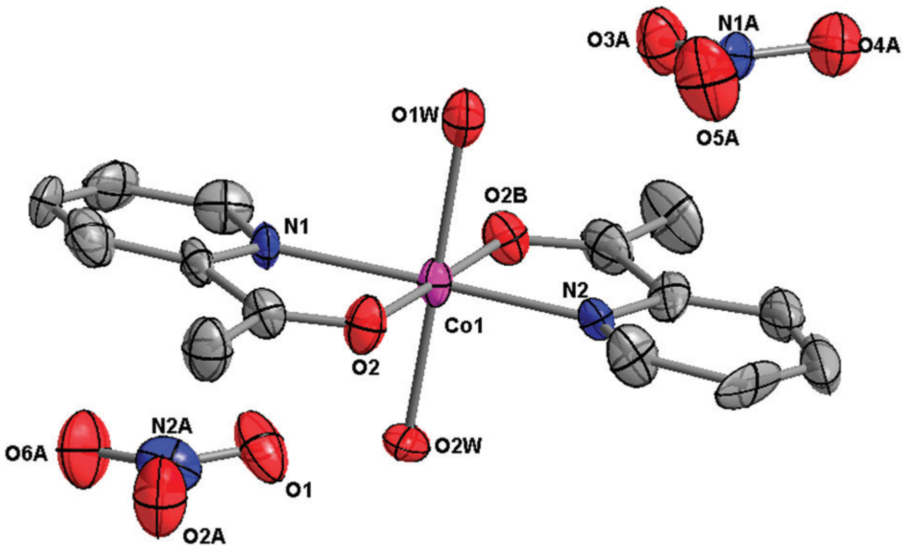

Figure 1. The thermal ellipsoid drawing (50% probability level) of the coordination environment of $[Co(2\text{-}Acpy)_2(H_2O)_2]^{2+}$.

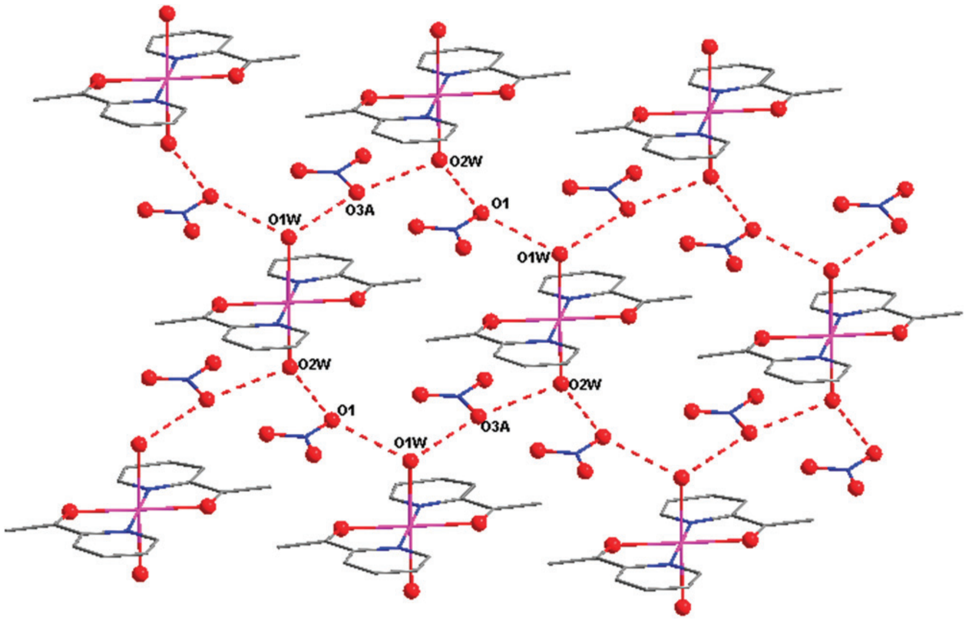

Figure 2. Packing diagram showing the hydrogen bond interactions established between water and nitrates.

environment at cadmium (figure 4). Nitrates and acetylpyridines are *cis* to each other as found for $[Cd(NO_3)_2(C_5H_4NCOOEt)_2]$ [17].

The Cd1–N2 bonds (2.3177(15) Å) are of the same order as those found for complexes formed by ethyl picolinate with cadmium(II) nitrate (2.363(4) Å) [17] or

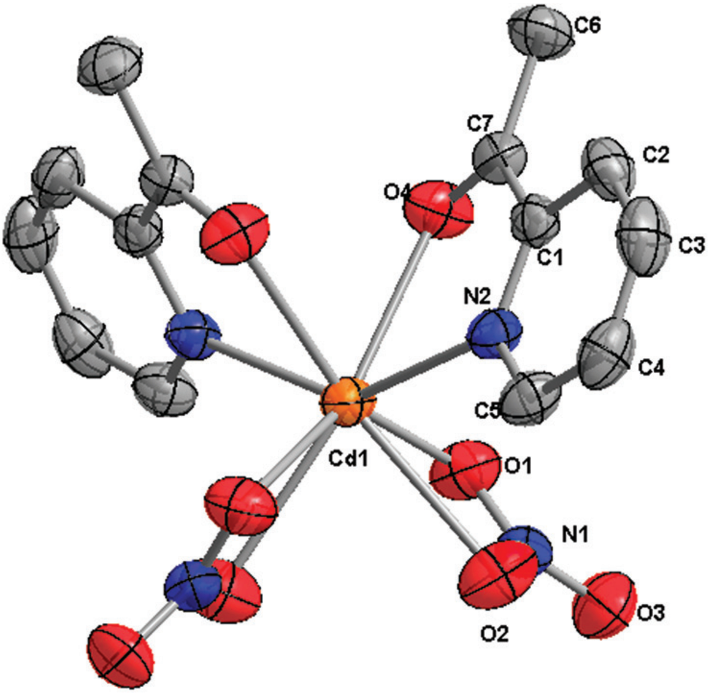

Figure 3. View of the molecular structure of $[Cd(2\text{-}Acpy)_2(NO_3)_2]$ in **3** (thermal ellipsoid at the 50% probability level).

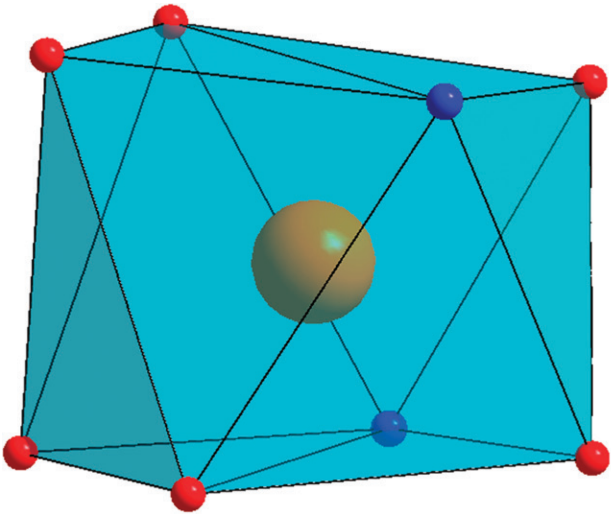

Figure 4. Coordination polyhedron of $[Cd(2\text{-}Acpy)_2(NO_3)_2]$.

$[CdI_2(C_5H_4NCOOMe)_2]$ (2.346 Å) [17], whereas the Cd1–O4 bonds (2.4919(16) Å) are approximately equal to ones found for these complexes (2.511(4) Å, 2.598 Å) [17]. Two oxygens of the bidentate nitrate are unsymmetrically bonded to the Cd1 center (Cd1–O1, 2.3291(18) Å, Cd1–O2, 2.5649(19) Å).

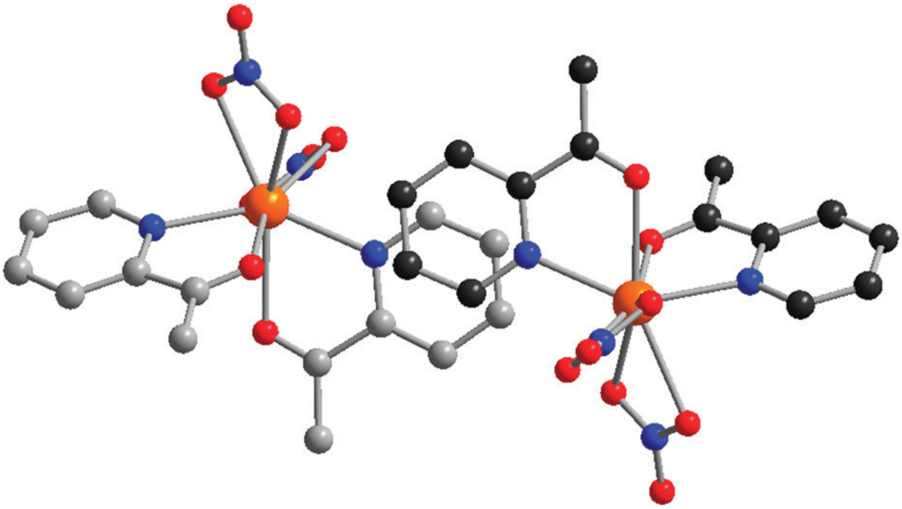

Figure 5. Intermolecular π–π stacking interactions in **3**.

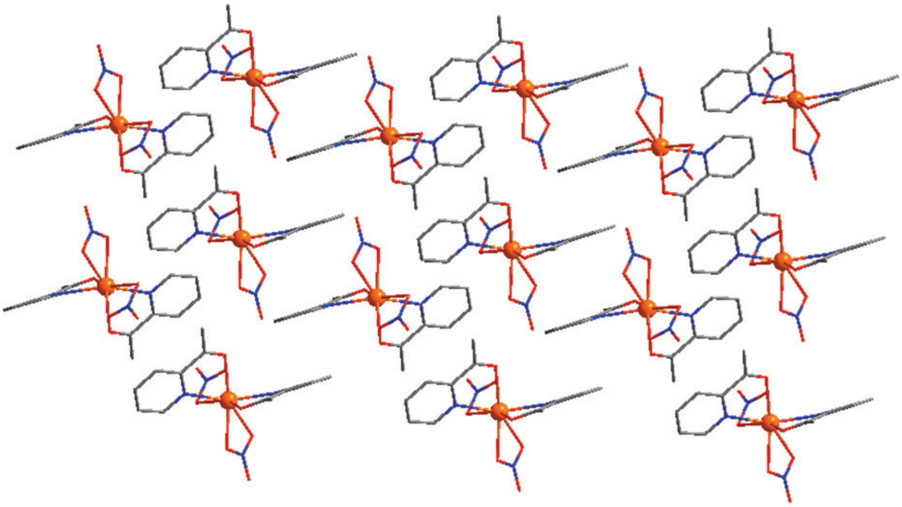

Figure 6. Packing diagram for **3** showing the π–π stacking interactions.

Analysis of the crystal structure at the supramolecular level reveals intermolecular π–π stacking interactions between aromatic rings belonging to the acetylpyridine ligands (figure 5), linking monomeric units in infinite chains (distances between the rings 3.3–3.7 Å). The packing diagram for **3** is shown in figure 6.

3.3. *IR spectroscopy*

The IR spectra for **1** and **2** were similar, displaying characteristic bands of 2-acetylpyridine N, O coordinated [very strong peaks at 1660 and 1656 cm^{-1} for

ν(CO), 1600 and 1598 cm^{-1} for ν(C=N + C=C) pyridine ring, strong peaks], a broad and intense band at 3216 and 3225 cm^{-1}, respectively, characteristic for O–H stretching from coordinated water, and the very strong free nitrate bands at 1384 cm^{-1} [22].

For **3**, the IR spectrum exhibits, apart from the characteristic bands of the N, O coordinated acetylpyridine ligand [1678 cm^{-1} for ν(CO), very strong peak, 1592 cm^{-1} for ν(C=N + C=C) pyridine ring, strong peak], the presence of bidentate nitrate with strong bands at 1445 and 1283 cm^{-1} assigned to ν_4 and ν_1 vibration modes of the nitrate group, respectively. The magnitude of splitting ($\nu_4 - \nu_1$) is 162 cm^{-1}, typical for bidentate bonding of nitrates [23]. Moreover, the ($\nu_4 + \nu_1$) region of the spectrum contains two weak bands at 1765 and 1729 cm^{-1} supporting this assignment [23]; ionic nitrate is not observed.

3.4. *Electronic spectroscopy*

The solid-state electronic spectrum of **1** consists of bands at 27,550, 21,740 and 9970 cm^{-1} characteristic for six-coordinate Co(II), assigned to $n \rightarrow \pi^*$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (ν_1) transitions [24]. The value of the magnetic moment determined at room temperature is 4.29 BM.

UV–Vis spectrum of **2** shows three bands at 26,810, 15,150 and 10,380 cm^{-1}, commonly assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transitions of a six-coordinate Ni(II) [24]. The value of the magnetic moment is 2.97 BM at 294 K.

4. Conclusions

We synthesized and characterized three new complexes of 2-acetylpyridine with Co(II), Ni(II) and Cd(II) nitrates. All compounds were characterized by elemental analysis, IR and UV–Vis spectroscopy. The structural determination of **1** and **3** was accomplished by X-ray diffraction. The ligand is N, O bidentate in all complexes. Co(II) and Ni(II) are six-coordinate with slightly distorted octahedral and cadmium is eight-coordinate. In this complex the cadmium is surrounded by two bidentate N, O acetylpyridine ligands and two bidentate coordinating nitrate anions, leading to a dodecahedral coordination environment. Only two Cd(II) complexes with two-coordinate nitrate have been reported, our compound is the third [17, 18].

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers: 684853 & 684854. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/deposit (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge

CB2 1EZ, UK; Tel: (44) 01223 762910; Fax: (44) 01223 336033; Email: deposit@ccdc.cam.ac.uk).

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